

Fig. 3.1. Raw materials used throughout the world to manufacture ammonia and nitrogenous fertilizers produced from ammonia. In the United States, 95 percent of the hydrogen required is based on natural gas or other hydrocarbons. [*Chem. Eng. Prog.* 49 (11) 63 (1963).]

countries use over 200 kg/ha of mixed fertilizers (N + P₂O₅ + K₂O), many others well below 25 kg/ha. Presumably all countries could profit by more extensive use.

RAW MATERIALS. Air, water, hydrocarbons, and power are the usual materials used. Coal can replace the hydrocarbons, but the process is more complex and expensive. See Fig. 3.1.

SYNTHETIC AMMONIA

USES AND ECONOMICS. Ammonia is a major raw material for industry and agriculture as shown in Table 3.1. The total tonnage consumed in the United States exceeded 19×10^6 t in 1981.¹ Nitric acid production uses 20 percent of production, urea 20 percent, and ammonium phosphates 15 percent. The uses are 80 percent in fertilizers, 20 percent in plastics and fibers, and 5 percent in commercial and military explosives. Commercial grades include essentially pure liquid NH₃ and aqueous ammonia, usually standardized at 28% NH₃. Cylinders and tank cars move much material, but pipelines over 1000 km long extend from production to distribution centers. Table 3.2 shows the major nitrogen-containing compounds produced in the U.S.

REACTIONS AND EQUILIBRIUMS. For the reaction



an equilibrium constant can be expressed as

$$K_p = \frac{p_{\text{NH}_3}}{p_{\text{N}_2}^{1/2} \times p_{\text{H}_2}^{3/2}}$$

Because the product molecule, ammonia, has a lower volume than the reactant molecules, the equilibrium yield of ammonia is increased by increasing pressure (Fig. 3.2). Temperature increase produces the opposite effect on the equilibrium, but increases the rate of reac-

¹t = 1000 kg.

Table 3.1 Ammonia and Ammonia Compounds Produced in the United States (in thousands of metric tons of contained nitrogen)

Compound	1970	1975	1976	1979	1980	1981
Ammonia, synthetic	10,335	12,353	12,492	13,924	14,686	14,225
Ammonium compounds, coking plants						
Ammonia liquor	11	11	4	6	6	na*
Ammonium sulfate	115	118	101	87	75	na
Ammonium phosphates	8	8	na	na	na	na
Total	10,469	12,490	12,597	14,017	14,767	14,225

*na = not available.

SOURCE: *Minerals Yearbook 1981*, Dept. of the Interior, 1982.

NOTES: 14,255,000 t of contained nitrogen = 17,310,000 t of 100% ammonia. At the last available census, there were 40 producers of ammonia in the United States, some with several plants, many shut down. The largest plant has a capacity of 1500 t/day.

tion greatly. This negative temperature effect on equilibrium combined with a strong positive effect on rate is common to many other reactions and requires a nice balance of conditions to assure good operating conditions and to make profits possible. Greater rate means reduced equipment size and consequent equipment cost.

RATE AND CATALYSIS OF THE REACTION. To keep equipment size small, the rate of the reaction must be increased substantially, since hydrogen and nitrogen alone react together extremely slowly. Commercial syntheses require an efficient catalyst to increase reaction rate to an acceptable figure. Ammonia catalysts of several types have been tested, but plants now use iron with added promoters—oxides of aluminum, zirconium, or silicon at about 3% concentration and potassium oxide at about 1%. These prevent sintering and make the catalyst more porous. For a given rate of gas flow, if pure iron produces 3 to 5 percent conversion, singly promoted iron can produce 8 to 9 percent and doubly promoted iron 13 to 14 percent. New catalysts are claiming concentrations near 25%. Iron catalysts lose their activity rapidly if heated above 520°C. Catalysts are also deactivated by contact with copper, phosphorus, arsenic, sulfur, and carbon monoxide, which alter the iron composition. This causes much trouble and expense in purifying the gases for the reaction. Chapter 6 discusses the purification of synthesis gases. Catalysts sufficiently robust to withstand higher levels of impurities and effective at lower temperatures (permitting higher equilibrium conversions) would be most valuable.

The exact mechanism by which the catalyst functions is not entirely clear, but certainly

Table 3.2 Major Nitrogen-Containing Compounds Produced in the United States (in thousands of metric tons)

Compound	1972	1975	1978	1979	1980	1981
Acrylonitrile	506	636	796	917	832	912
Ammonium nitrate	6255	6955	6,555	7,539	8,297	7,992
Ammonium sulfate	2246	2545	2,636	2,253	2,033	1,919
Ammonium phosphates	5908	6727	10,470	10,984	12,162	11,037
Nitric acid	7255	7545	7,213	8,105	8,392	8,218
Urea	3191	3445	5,703	6,364	7,118	6,918

SOURCE: *Minerals Yearbook 1981*, Dept. of the Interior, 1982.

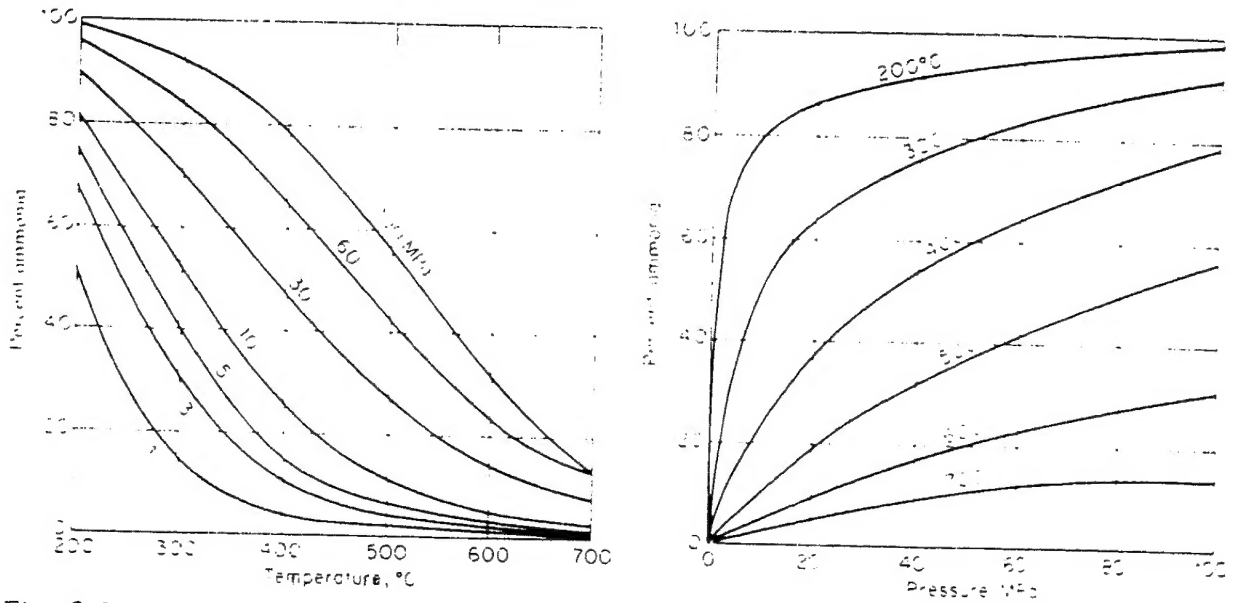


Fig. 3.2. Percentage of ammonia at equilibrium from an initial mixture of 3:1 H_2 : N_2 gas at various temperatures and pressures. (Comings, *High Pressure Technology*, p. 410. Compare Frear and Baber, *ECT*, 2d ed., vol. 2, 1963, p. 260.)

the N and H either react chemically with the surface or are adsorbed, then migrate, probably forming H, N, NH, NH_2 , and NH_3 in that order, followed by desorption.

Space velocity is the volume of gases, corrected to standard conditions (0°C and 101 kPa) that pass over one volume of catalyst per unit time. Of course, the percentage of ammonia produced at a given temperature and pressure and for a given catalyst decreases with increasing space velocity. Different commercial plants have varying space velocities, reflecting the differences in catalysts and reactors. Most industrial units use a space velocity between 10,000 and 20,000 per hour.

MANUFACTURING PROCEDURES. Manufacturing consists essentially of six phases (see Fig. 3.3): (1) manufacture of reactant gases, (2) purification, (3) compression, (4) catalytic reaction, (5) recovery of ammonia formed, and (6) recirculation. Cost is greatly influenced by the pressure, temperature, catalyst, and raw materials used. Of most current interest is heat recovery and reuse. Different groups have developed procedures satisfactory for their local

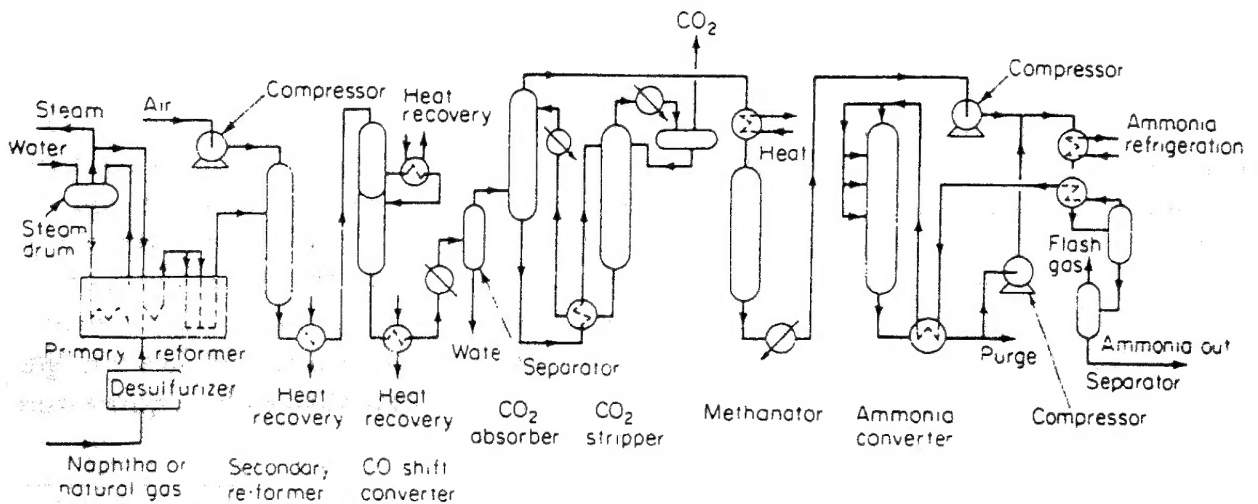


Fig. 3.3. The Kellogg ammonia process. (M. W. Kellogg Co.)

conditions. The elimination of intermediate storages, single train construction, and the use of rotary (replacing reciprocating) compressors have made the capacity of today's plants much larger (up to 1650 t/day) than those of yesterday. The greatly increased cost of energy has made them more complex because of the need to conserve energy. In 1950, 55.9 GJ/t were required to make ammonia, this has been reduced to 26 in 1982 and continues to fall. Many plants produce steam for outside use while requiring little power as input. These factors and extreme worldwide competition have kept ammonia prices low.

There is as much difference in the economical sources of hydrogen as any variable. The principal hydrogen-manufacturing process in the United States in 1982 was a combination process in which natural gas, air, and steam were reacted with the addition of heat over a catalyst to produce a 3:1 mixture of hydrogen and nitrogen along with carbon dioxide and water. The carbon dioxide and water were then removed. Synthesis gas production is detailed in Chap. 6. Other systems used in some areas are: electrolysis of water (a pressure process is being developed^{1a} that may be competitive soon), by-product hydrogen, cracking of hydrocarbons, coal-water and hydrocarbon-water interactions, and partial oxidation of hydrocarbons. There are also many totally untried (commercially) ideas being put forward.

SYNTHESIS SYSTEMS. All ammonia syntheses are based on the overall reaction (1) shown earlier. This reaction is quite exothermic, so the design of the converter (Fig. 3.4) must protect the unit from overheating, both to ensure control at the optimum temperature for conversion and to protect the shell against metallurgical deterioration at the high pressure and temperature. The flowchart of Fig. 3.3 illustrates the basic steps of a current system.

Ammonia synthesis gas is prepared by high-pressure catalytic reforming of hydrocarbon feed, usually natural gas freed of sulfur, in the presence of steam over a nickel catalyst in the primary reformer, then subjected to a catalytic "shift" at a lower temperature in the presence of air in one or more secondary reformers. The shift reaction serves two purposes—(1) it produces more hydrogen per unit of fuel, and (2) it oxidizes much of the carbon monoxide to the more easily removed carbon dioxide. It has become customary to add an oversize charge to the low-temperature-shift catalyst bed. This "guard" catalyst captures sulfur and chlorine poisons and extends the main catalyst's life over 100 percent. After CO₂ removal by water and then chemical absorption, any residual CO and CO₂ is completely converted to methane in the methanator. Methane is an inert gas with respect to the ammonia catalyst. Throughout the entire process, conservation and reuse of heat is so vital that it has been said that an ammonia plant is really a steam generating plant that incidentally produces ammonia. Much more steam than ammonia is made (4:1).

After catalytic methanation at about 2.75 MPa, the 3:1 hydrogen-nitrogen mixture, freed of carbon-containing compounds except for a little methane, is raised to the full reaction pressure of about 20 MPa by means of a (usually) turbine-driven centrifugal compressor. Various methods of temperature regulation are used in the converters: heat exchange coils are inserted or cold gas injected between beds. The ammonia is then recovered by means of refrigeration or absorption and handled as an anhydrous liquid under modest pressure.

After the ammonia is removed, the remaining gases are far too valuable to discard. They contain all the inerts fed to the system (CH₄, Ar, Ne, etc.) at the highest concentration anywhere in the system. The concentration of inerts is, therefore, regulated by removing (purging) some of this gas continuously. When fuel was quite cheap, this gas was burned, but it is now stripped of its undesirables and reused.

^{1a}daRosa, A Compressorless Ammonia Process, *CHEMTECH* 118 (1) 28 (1978).

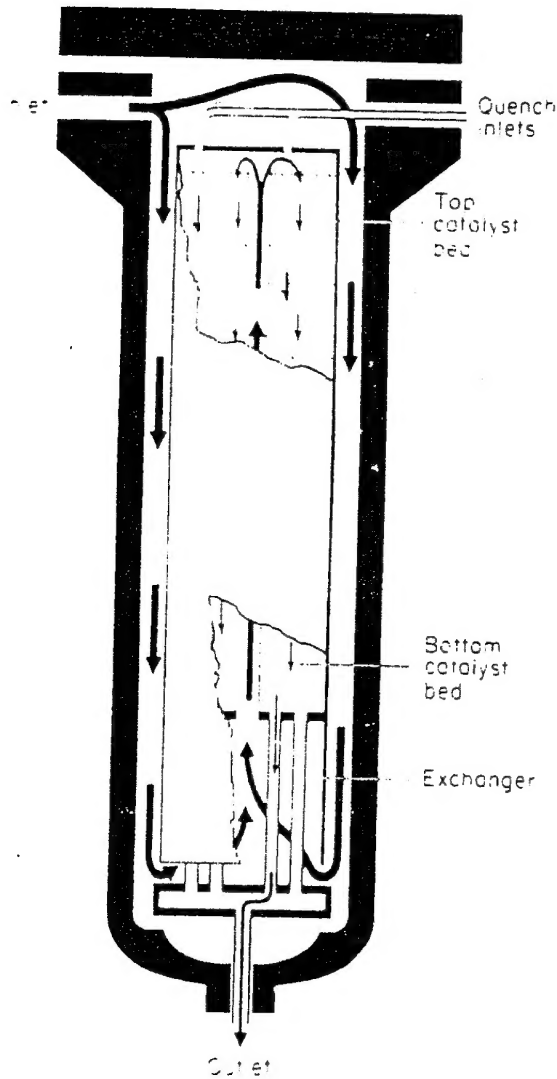


Fig. 3.4. Ammonia-synthesis converter. The converter consists of a high-pressure shell containing a catalyst section and a heat exchanger. The catalyst section is a cylindrical shell which fits inside the pressure shell, leaving an annular space between the two. The catalyst section contains several beds supported on screened grids. To maintain the catalyst at optimum temperature for maximum yield, cold feed-gas quench is injected before each catalyst bed. The top bed contains the smallest quantity of catalyst. Since the temperature gradient is flatter in succeeding beds, bed sizes are graduated, with the largest bed at the bottom. Beneath the catalyst section is the heat exchanger. This preheats fresh inlet gas against hot reacted gas from the last catalyst bed. The top quench point permits the introduction of feed gas without preheating and provides temperature control to the first catalyst bed.

The feed gas enters at the top of the converter and flows downward between the pressure shell and the wall of the catalyst section. The gas cools the shell and is heated. The gas then enters the exchanger at the bottom of the converter and, by circulating around the exchanger tubes, is further preheated against

hot effluent. Some feed gas is introduced directly to the top of the first bed, where it meets the preheated feed. The combined stream at a temperature of 370 to 425°C is then introduced into the top catalyst bed. The gas passes downward through the catalyst, with a rapid temperature rise as the ammonia reaction proceeds, and then through the catalyst supporting grid into a space between the first and second beds. Here the temperature is reduced and the ammonia content diluted by injection of cold feed gas. This permits control throughout the catalyst beds to obtain optimum temperatures for maximum yields. In a like manner, the gas flows downward through the lower catalyst beds (M. W. Kellogg Co.)

In the 1970s, a revolution in ammonia manufacturing came about as the reciprocating compressors common at that time were replaced by centrifugal units. At that time, the ammonia process was regarded as highly efficient, a mature process, but careful examination of the process step-by-step and the severe economic pressure led to major improvements and cost drops approaching 50 percent. Some of the important changes made are summarized below.

1. When operating procedures were carefully studied, it became possible to operate without duplication of equipment (single train) and to eliminate intermediate storage.
2. Quality catalysts made it possible to operate economically at the lower pressures at which centrifugal compressors are most economical. Higher pressures were used when only reciprocating units were available.

3. Large capacity compressors, better catalysts, and better converters made larger units attractive and permitted many economies that were a result of the larger size.

4. By raising the temperature of the primary reformer outlet and preheating the air to the endothermic secondary reformer, manufacturers reduced the overall cost of reforming. Primary re-formers operate at very high temperatures, so they are far more expensive than secondary ones. Shift reactors are now commonly two-stage.

5. Digital computer control of process variables has narrowed the range of variation and given consistently better operation at nearer to maximum conditions.

6. Most carbon dioxide is removed by absorption in water, but the final stripping requires the use of an alkaline reagent. Three processes compete: (a) inorganic absorbents (usually K_2CO_3), (b) organics (mainly amines), and (c) "physical" absorbents (Fluor's propylene carbonate). The choice is made based on residual CO_2 level, effect of impurities, and problems of regeneration.

7. Bleed gas from the synthesis loop, formerly burned, is now recovered with substantial reduction (near 15 percent) in energy requirement per unit of product. Cryogenic separation (Petrocarbon Co.) recovers hydrogen and some nitrogen. Gaseous diffusion² through hollow fibers (Monsanto's Prism) recovers hydrogen only. With the Prism process the two separated streams are, typically, 89% hydrogen, 6% nitrogen, 5% inerts and 20% hydrogen, 42% nitrogen, and 38% inerts. It is also possible to separate inerts, usually by scrubbing with nitrogen, before gas enters the synthesis loop (Braun); this makes possible a much smaller purge. A completely different approach uses a pressure swing molecular sieve system after the high-temperature shift reaction to produce a highly purified hydrogen feed. This eliminates the secondary reformer and no air is added to the system, so nitrogen must be obtained by air distillation or some similar process.

8. Synthesis converters are now highly developed and vastly improved over previous designs. Both horizontal and vertical types are used with cooling by quenching, a common practice, but some cooling with tubular inserts is also done.³ Inlet gases conventionally pass along the shell, being preheated and reducing the maximum shell temperature. Low pressure drop is desirable to reduce operating costs; small catalyst size reduces required catalyst volume (high area-to-volume ratio). Most conversion occurs in the first bed, for there the driving force toward equilibrium is greatest. Designs of axial and radial flow converters from 500 to 1600 t/day are available. Modern designs use pressures of 15 to 30 MPa at around 500°C. Outlet concentrations of ammonia are 16 to 25%.

9. Low-cost ammonia recovery from converter outlet gases has several options. Multiple-stage refrigeration combined with some reduction in pressure is usually used. If cooling water is very cold, some water condensing may be possible. Where markets are nearby, a water wash to produce aqua ammonia may be desirable. Excess steam may be used to run an absorption refrigeration system to condense the ammonia. The problem is one of cost.

COST. The method of production of the hydrogen and the feedstock selected are the major items influencing the final cost of the ammonia produced. Much effort is currently being exerted to reduce costs by reducing steam and fuel requirements. Presently operating plants use 40 to 45 GJ per metric ton of ammonia produced. With simplified processing procedures, improved catalysts, and operation at pressures low enough to permit a one-stage compressor,

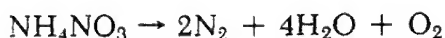
²Ricci, Tightening the Loop in Ammonia Manufacture, *Chem. Eng.* 86 (3) 54 (1979).

³Forster, Improved Reactor Design for Ammonia Synthesis, *Chem. Eng.* 87 (18) 62 (1980).

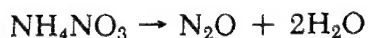
energy use can theoretically be reduced to 21 GJ per metric ton. Plants designed to produce ammonia at 27 GJ per metric ton are currently available, but the current unfavorable economic conditions have prevented construction of such plants and reduced the retrofitting of improvements.

AMMONIUM NITRATE

Ammonium nitrate is a very important nitrogenous fertilizer because of its high nitrogen content (33%), the simplicity and cheapness of its manufacture, and its valuable combination of quick-acting nitrate and slower-acting ammoniacal nitrogen. Its tendency to cake on storage reduced its acceptability at first but proper granulation, the addition of antihygroscopic agents, and better packaging have largely remedied this problem. Most commercial and many military explosives contain cheap ammonium nitrate as the major explosive ingredient. Ammonium nitrate is difficult to detonate, but, when sensitized with oil or mixed with other explosive materials, it can be detonated with a large booster-primer. Ammonium nitrate mixtures are "permissibles," that is, permitted for use in coal mines where combustible vapors may be encountered. The use of explosives in mines and quarries provides a large and continuing market. Amatol is a mixture of TNT and granular ammonium nitrate (AN). This is the major conventional military explosive. On explosive decomposition, AN rapidly and violently decomposes to form elemental nitrogen.



Under different conditions, i.e., at 200 to 260°C, it is safely decomposed to form the anaesthetic nitrous oxide. This is the commercial method of preparation.



Ammonium nitrate is made by reacting nitric acid (made by oxidizing ammonia) with ammonia:



If properly proportioned and preheated, the reaction can be run continuously to produce molten ammonium nitrate containing very little water (1 to 5%) which can be formed into small spheres (prills) by dropping the reaction product through a shot tower or into flakes by cooling it on belts or drums. By fluidized bed treatment, it is possible to obtain a dry granular material as product. Batch processes have also been used, but the labor and equipment costs are prohibitive. Figure 18.5 shows a typical flowchart.

AMMONIUM SULFATE

Ammonium sulfate, which has little tendency to cake on storage, was accepted by farmers long before ammonium nitrate was made noncaking. Originally it was made by using sulfuric

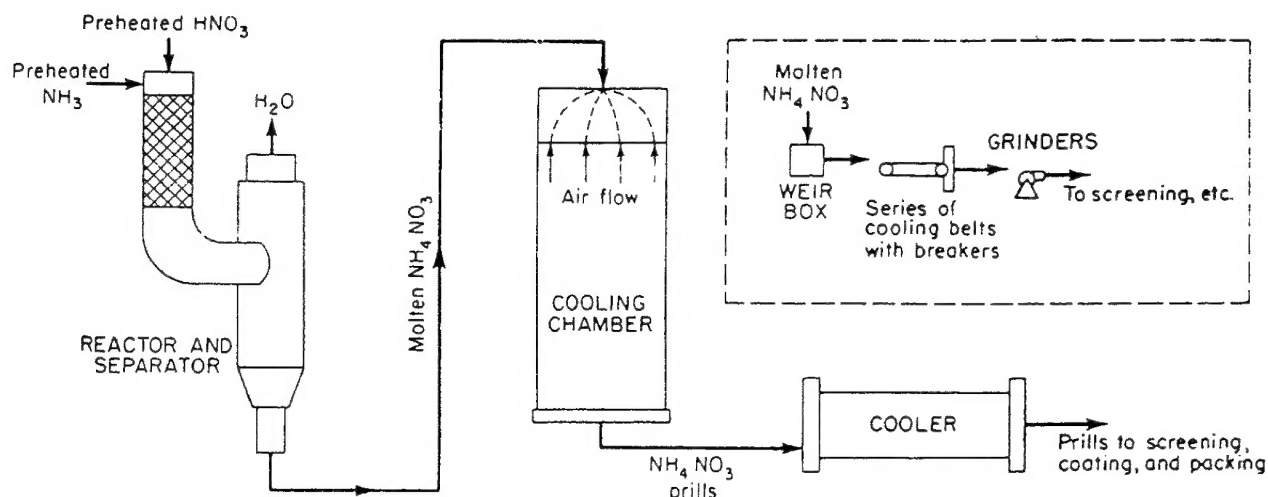
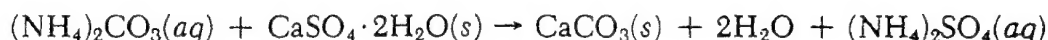


Fig. 3.5. Simplified flowchart for the Stengel process for ammonium nitrate manufacture. (*Commercial Solvents Corp. and L. A. Stengel.*)

acid to scrub by-product ammonia from coke-oven gas, and much is still produced in this manner. However, most ammonium sulfate is now made by reaction between synthetic ammonia and sulfuric acid. Production is about 2.3×10^6 t/year with about 20 percent from by-product ammonia. Where sulfur for sulfuric acid is at a premium, for example at Sindri, India, a process based on gypsum and carbon dioxide from combustion is used:



Anhydrite can also be used. Some ammonium sulfate is also obtained as a by-product of caprolactam (for nylon-6) manufacture.

AMMONIUM PHOSPHATES

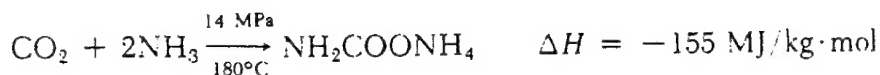
There are three possible ammonium orthophosphates, only two of which are manufactured on any scale. Monoammonium phosphate (MAP) is readily made by reacting ammonia with phosphoric acid, centrifuging, and drying in a rotary dryer. It is used in quick-dissolving fertilizers and as a fire-retarding agent for wood, paper, and cloth. Diammonium phosphate (DAP) requires a two-stage reactor system in order to prevent loss of ammonia. A granulation process follows with completion of the reaction in a rotary drum.

UREA

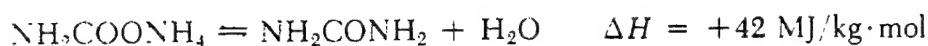
Urea is in many ways the most convenient form for fixed nitrogen. It has the highest nitrogen content available in a solid fertilizer (46%). It is easy to produce as prills or granules and easily transported in bulk or bags with no explosive hazard. It dissolves readily in water. It leaves no salt residue after use on crops and can often be used for foliar feeding. In addition to fertilizer use, it is used as a protein food supplement for ruminants, in melamine produc-

tion, as an ingredient in the manufacture of resins, plastics, adhesives, coatings, textile anti-shrink agents, and ion-exchange resins. It is an intermediate in the manufacture of ammonium sulfamate, sulfamic acid, and phthalocyanines. Annual production in the United States is very large, 6.4×10^6 t at \$150 to \$160 per metric ton in 1982.

Two reactions are involved in the manufacture of urea. First, ammonium carbamate is formed under pressure by reaction between carbon dioxide and ammonia



This highly exothermic reaction is followed by an endothermic decomposition of the ammonium carbamate



Both are equilibrium reactions. The formation reaction goes to virtual completion under usual reaction conditions; the decomposition reaction is less complete. Unconverted carbon dioxide and ammonia, along with undecomposed carbamate, must be recovered and reused. This is a troublesome step. The synthesis is further complicated by the formation of a dimer called biuret, $\text{NH}_2\text{CONHCONH}_2 \cdot \text{H}_2\text{O}$, which must be kept low because it adversely affects the growth of some plants.

Once-through operation was once practiced with the unchanged ammonia converted to ammonium compounds, but this is now too expensive, and the markets for the secondary products are problematical. Partial and total recycle plants have been built, but only total recycle plants are considered now.

The conventional plant decomposes the carbamate in one or more decomposers, each at a lower pressure than the previous one. All evolved gases must be repressured to the reactor pressure, and this is expensive. Presently the most popular method is designed to minimize the use of energy by "stripping" the product liquor by contacting it with incoming carbon dioxide and by using some of the heat of formation of carbamate to bring about the endothermic decomposition and the rest to generate process steam. Figure 3-6 shows a flowchart for the process. Liquid ammonia, gaseous carbon dioxide, and recycle materials meet in a heat exchanger-reactor at a pressure of 14 MPa at 170 to 190°C to form carbamate with most of the heat of reaction carried away as useful process steam. The carbamate decomposition reaction is both slow and endothermic. The mix of unreacted reagents and carbamate flows to the decomposer. The stoichiometric ratio of CO_2/NH_3 conversion to urea is essentially about 55 percent, but by using an excess of CO_2 (or NH_3), the equilibrium can be driven as high as 85 percent. The reactor must be heated to force the reaction to proceed. The flowchart shows a decomposer followed by a stripper in which CO_2 is introduced; these are at substantially identical pressures, requiring no gas recompression—only a small liquid recycle pump. For all the unreacted gases and undecomposed carbamate to be removed from the product, the urea must be heated at lower pressure (400 kPa). The reagents are reacted and pumped back into the system. Evaporation and prilling or granulating produce the final product. Overall, over 99 percent of both CO_2 and NH_3 are converted to urea, making environmental problems minimal. Carbamate is highly corrosive to both ordinary and stainless steels, but with oxygen present, 300 series stainless steels resist it very well, so some air is introduced along with the CO_2 reagent to reduce system corrosion.

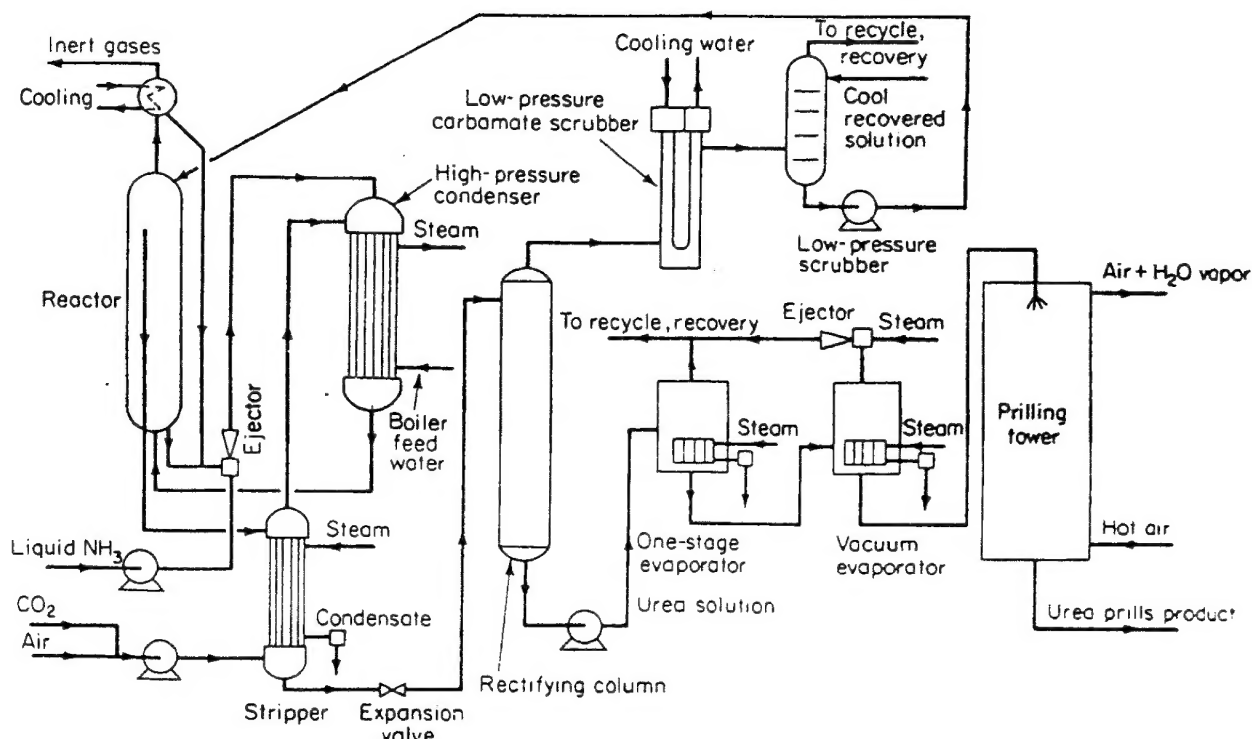


Fig. 3.6. Simplified flow chart, Stamicarbon urea stripping process. (Stamicarbon and M. W. Kellogg Co.)

NITRIC ACID

HISTORICAL. Nitric acid has been known and esteemed for a long time. Distillation of saltpeter with sulfuric acid is the usual ancient method of preparation. Lightning forms considerable amounts in the atmosphere.

Ammonia can be burned in air in the presence of a platinum catalyst, and the nitrogen oxides thus formed can be oxidized further and absorbed in water to form nitric acid. Cheap ammonia has made this process much less expensive than the older synthesis from Chilean saltpeter.

USES AND ECONOMICS. Most nitric acid is used in making ammonium nitrate. The manufacture of other organic and inorganic nitrates along with organic nitro compounds uses substantial quantities. Sodium, copper, and silver nitrates are produced on a large scale. Direct applications include photoengraving, metal pickling and passivating, and the parting of gold and silver.

Phosphate rock for fertilizer use has its phosphorus made available for plant use by acidulation with sulfuric acid. Acidulation with nitric acid adds desirable nitrogen fertilizer to the phosphorus already present. Nitric acidulated fertilizer cakes on storage, but this difficulty is gradually being overcome; this market is potentially large.

Organic nitrates (nitroglycerine, glycol nitrate, cellulose nitrates) and nitro compounds (TNT, RDX, picric acid) all require nitric acid for their synthesis. Nitroparaffins are also made on a large scale by vapor phase nitration with nitric acid. Nitric acid's strong oxidizing characteristics in dilute solutions, usually highly objectionable in organic syntheses, are sometimes most useful.

Commercial grades are made to specification, usually from 36 to 42°Bé (53.4 to 68.7% w/w). Highly concentrated acid (94.5 to 95.5%) known to the trade as "concentrated" acid is made in specially designed plants and is more expensive. It can be made from weaker acid by extractive distillation with strong dehydrating agents such as sulfuric acid and magnesium sulfate.

RAW MATERIALS. Ammonia, air, water, and platinum-10% rhodium gauze catalyst are the essential materials. Location near an ammonia plant is usually desirable. Since it requires only 17 kg of ammonia to contain 1 kg-atom of nitrogen, but 105 kg of 60% nitric acid, it may be cheaper for large users to ship ammonia rather than nitric acid. Stainless-steel cars and trucks handle nitric acid solutions.

REACTIONS AND ENERGY CHANGES. The following reactions have been observed as of major importance in nitric acid manufacture:

	ΔH , kJ/kg·mol
(overall) $\text{NH}_3(g) + 2\text{O}_2(g) \rightarrow \text{HNO}_3(aq) + \text{H}_2\text{O}(l)$	-437 (1)
$4\text{NH}_3(g) + 5\text{O}_2(g) \rightarrow 4\text{NO}_2(g) + 6\text{H}_2\text{O}(g)$	-227 (2)
$2\text{NO}(g) + \text{O}_2(g) \rightarrow 2\text{NO}_2(g)$	-57.1 (3)
$3\text{NO}_2(g) + \text{H}_2\text{O}(l) \rightleftharpoons 2\text{HNO}_3(l) + \text{NO}(g)$	-55.7° (4)
$4\text{NH}_3(g) + 3\text{O}_2(g) \rightarrow 2\text{N}_2(g) + 6\text{H}_2\text{O}(g)$	-317 (5)
$4\text{NH}_3(g) + 6\text{NO}(g) \rightarrow 5\text{N}_2(g) + 6\text{H}_2\text{O}(g)$	-451 (6)
$2\text{NO}_2(g) \rightarrow \text{N}_2\text{O}_4(g)$	-28.7 (7)

Varies with HNO_3 concentration.

Gaseous mixtures of oxides of nitrogen (NO , N_2O_3 , NO_2 , N_2O_4) are commonly referred to as NOX regardless of composition.

Manufactured acid contains some nitrous acid (HNO_2) when the concentration is between 20 and 45% HNO_3 w/w and dissolved N_2O_4 when the concentration is over 55%. The oxidation potential of 20 to 45% acid stabilizes trivalent nitrogen (HNO_2), over 55% stabilizes tetravalent nitrogen (N_2O_4).

Reaction (2) is a swift (when catalyzed) reaction, complete in less than a millisecond. It must, therefore, be run as an adiabatic reaction. The concentration of ammonia feed must be limited so that the maximum temperature reached does not damage sive catalyst.

Reaction (3) is a slow, gas-phase reaction with third-order kinetics and a rate that increases with increasing temperature. Complete conversion to NO_2 is not commercially feasible.

Reaction (4) shows several troublesome features despite its fair speed and the relatively small ΔH . Approach to equilibrium is reasonably rapid, but the equilibrium is shifted to the left. If the acid is too concentrated or too hot, the reverse reaction occurs. The equilibrium for reaction (4) as a plot of $\log(p_{\text{NO}}/p_{\text{NO}_2}^3)$ in the gas phase and the equilibrium in the liquid phase with temperature as a parameter. The absorption reaction is more complicated than (4) indicates, for NO_2 , N_2O_3 , N_2O_4 , and HNO_2 are all

⁴Theobald, Messungen zum Gleichgewicht Salpetersauren/Nitrose Gase, *Chem. Ing. Tech.* **40** (15) 763 (1968).

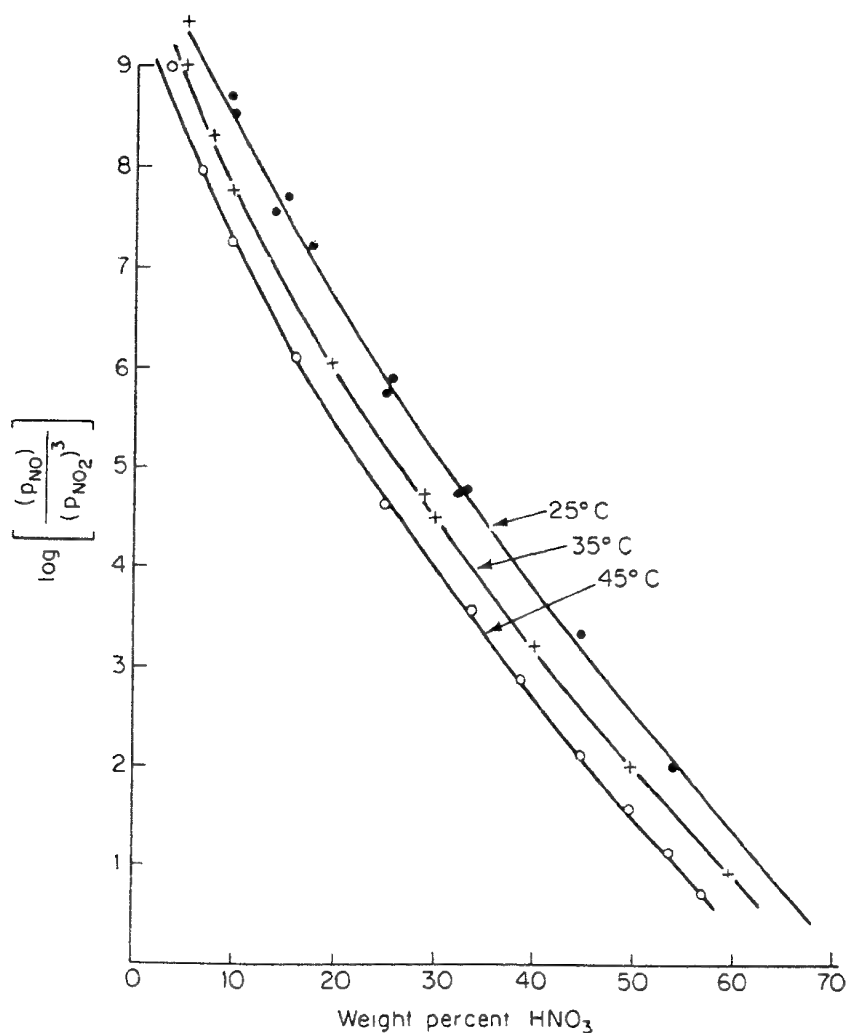


Fig. 3.7. An equilibrium constant for nitric acid manufacture.

to produce HNO₃, but one-third of all such dissolved gases are then expelled as NO, requiring reoxidation and reabsorption until the quantity of NO remaining is very small. This is a time-consuming process.

MANUFACTURING PROCEDURES. Originally the whole oxidation-absorption-reoxidation-reabsorption process operated at atmospheric pressure. Such plants are expensive because the equipment is large. Atmospheric pressure plants cannot produce acid stronger than 50 to 55% HNO₃. Such plants are not now being considered.

Two types of units dominate current production—single-pressure plants (commonly known as American or DuPont) and dual-pressure systems (called European). The single-pressure plant has lower capital cost and produces more by-product steam; the dual-pressure unit has a lower catalyst cost and a slightly higher yield. Currently, overall costs are almost exactly competitive.⁵

The Single-Pressure Process. The single-pressure process is shown in the flowchart of Fig. 3.8. A multiple-stage rotary compressor with intercoolers between stages is driven by a

⁵Harvin, Leray, and Roudier, "Single Pressure or Dual-Pressure Nitric Acid—An Objective Comparison," AIChE 71st Annual Meeting Preprint, 1978.

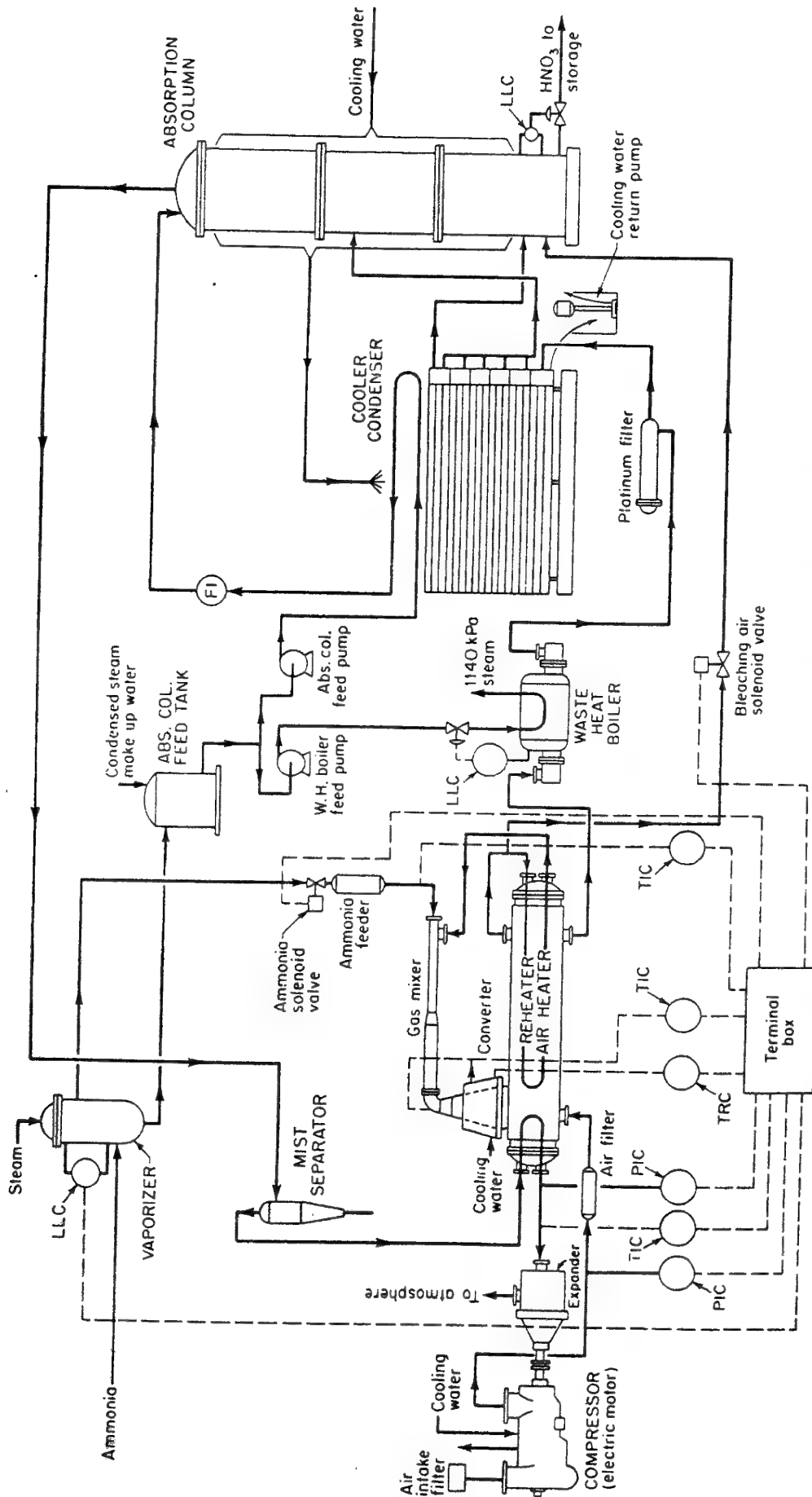


Fig. 3.8. Flowchart for the manufacture of 60% nitric acid from ammonia: DuPont high-pressure (10 MPa) self-sustaining 225-t/day unit. The expander turbine operates on the heat of the tail gas (essentially N_2). A high-efficiency platinum filter collects platinum volatilized or eroded and is essential to economic operation. LLC, liquid level indicating controller; FI, feed intake; LLC, liquid level indicating controller; PIC, pressure indicating controller; TIC, temperature indicating controller; TRC, temperature recording controller. (E. A. Rass, Chemical and Industrial Co.)

steam turbine and a power recovery turbine, the so-called "tail-gas expander." Stage inter-cooling is regulated to give an outlet temperature near 230°C at 1 MPa.

The outlet air is split, 85 percent going to the converter and 15 percent to heat exchangers and the bleach column. The hot compressed air is mixed with superheated ammonia and sent to the converter, which operates at 800 to 950 kPa. The air-ammonia mix, containing about 10% ammonia, passes through a stack of about 30 layers of 80 mesh platinum + 10% rhodium gauze. Combustion is rapid, with an exit temperature of 940°C. The conversion to NO is 94 to 95 percent and about 62 g of platinum alloy is required per metric ton of daily acid capacity. Gas temperature and ammonia concentration to the reactor are critical. Above 11.5 to 12% ammonia, explosion is possible. The entering gas must be at least 205°C, preferably 230°C, for the first layer of gauze to remain at reaction temperature, but the gauze temperature must not exceed 940°C or catalyst loss will be excessive. At 10% ammonia, the adiabatic temperature rise is 710°C, thus restricting the ammonia concentration to 10%. Catalyst life is 6 to 10 weeks, largely as a result of erosion. This causes a catalyst charge of approximately \$5 per metric ton of 100% HNO₃ produced. Cobalt trioxide-containing pellets are also being used and require less frequent replacement, but conversion is somewhat lower.

Converter exit gas is passed through a steam superheater, a waste heat boiler, and a tail gas preheater, emerging at about 200°C. It then passes into a cooler-condenser which produces 40 to 45% HNO₃ as product containing about 40% of the fixed nitrogen. Both cooled exit gas and dilute nitric acid pass on to the absorber, still under full pressure of 980 kPa. The absorber-reactor is a sieve plate or bubble cap unit with cooling coils on each of the 20 to 50 trays. Gas enters at the bottom, dilute nitric acid part way up the column, with cold water entering at the top. The temperature of the exit gas is near 10°C. Two pinch points caused by kinetic problems occur within the column. Near the bottom, the rate of reoxidation of evolved NO is slow because the strong acid present prevents rapid absorption of NO₂ causing slow evolution of NO. Near the top, the concentrations of NOX and oxygen become so low that the driving force for absorption is small.

The acid leaving the bottom of the column contains some NOX, mostly as N₂O₄ (colorless) but some as red NO₂. This is "bleached" by passing it through a column countercurrent to the 15% primary air (needed for oxidation of NO to NO₂) bled off from the air compressor. Some plants include the bleach section at the bottom of the main absorber column.

Chlorine impurity presents a unique problem in the absorber. Chlorides cannot leave through the bottom because the strong nitric acid oxidizes them to chlorine, which is swept up the column. They cannot leave in the top gas because here NO reduces them to HCl which goes down the column in the aqueous phase. The combination of HCl and HNO₃ is highly corrosive. Chlorides must, therefore be excluded from entry or provision made for their purging.

Air pollution problems are created because it is too expensive to try to absorb more than 97 to 98 percent of the NO leaving the gauze. U.S. federal air pollution regulations require 99.8 percent absorption. Three methods are currently used to meet requirements. (1) Stack gas is reheated to 680°C and reacted with natural gas. The combustion reaction between natural gas and NO increases the gas temperature and this increases the power recovered in the expander. (2) Reheated stack gas can be treated with ammonia or hydrogen (if available from a nearby ammonia plant) in a catalytic reactor to reduce the NO to N₂. The temperature rise is quite small. (3) Additional absorption capacity operating at low temperature (e.g., 5°C) can increase absorption sufficiently to meet requirements. The equipment will be very large, for the driving force for absorption will be quite small.

The Dual-Pressure Process. The dual-pressure process buys lower catalyst cost by using lower velocities, larger diameter catalyst beds with thinner gauze layers (only four), and oper-

ates with lower pressure, 240 kPa, in the converter. Gases then pass through heat recovery systems and are compressed to 990 kPa for absorption and bleaching. The rest of the process is similar to the single-pressure process.

The dual-pressure system reduces catalyst cost sharply to about \$1.50 per metric ton of 100% HNO_3 produced. It requires about 2 percent less power but recovers about 5 percent less power and produces less by-product steam compared with the single-pressure system. The weight of catalyst per unit of daily production is about the same for both processes.

Both processes give highly efficient production of the same quality product and yield effluent gases within the same pollution potential limits.

SODIUM NITRATE

Sodium nitrate has both fertilizer and industrial uses: fluxes, fireworks, pickling, heat-treating mixes, tobacco additive. In the highlands of Chile, great natural deposits occur, some 8 to 65 km wide and 0.3 to 1.2 m thick under a shallow overburden. Simple countercurrent leaching and crystallization produces a good quality product. For years these deposits dominated the world's fixed nitrogen supply. Much of the world's iodine is obtained as a by-product of NaNO_3 production. With lowered ammonia cost, reactions between salt or soda ash and nitric acid meet current needs at modest prices. Some plants respond more favorably to NaNO_3 than to competing nitrogen sources.

POTASSIUM NITRATE

Potassium nitrate is manufactured in two ways: (1) by reacting nitric acid with potassium chloride with a chlorine by-product, and (2) reacting sodium nitrate with potassium chloride and crystallizing out the salt. It is an excellent fertilizer with two useful fertilizing components—13% N, 44% K_2O . Other uses include explosives, ceramics, and heat-treating salts.

CYANAMIDE

At one time cyanamide was a useful agricultural fertilizer; later its major importance came from its derivative—dicyandiamide. Its use has now sharply diminished until only one small plant remains. Its production is of considerable historical interest because a large plant was built to produce it at the end of World War I, but it was never successful commercially. Earlier editions of this book give details of its production.

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Chapter 4

Sulfur and Sulfuric Acid

Sulfur is one of the most important and basic materials in the chemical process industries. It exists in nature both in the free state and combined in ores such as pyrite (FeS_2), sphalerite (ZnS), and chalcopyrite (CuFeS_2). It is also an important constituent of petroleum and natural gas (as H_2S). The largest application of sulfur is in the manufacture of sulfuric acid.¹

HISTORICAL. Sulfur has a history as old as any other chemical and has developed from the mystic yellow of the alchemist to one of the most useful substances in modern civilization. It was burned in early pagan rites to drive away evil spirits, and even then the fumes were used as a bleach for cloth and straw. For many years, a French company held a monopoly on sulfur by controlling the world supply from Sicily. Partly because of monopolistic high prices and partly because of the abundance of pyrites, elemental sulfur was little used in the United States prior to 1914. Though sulfur was discovered in the U.S. Gulf of Mexico region in 1869, it was difficult to mine because of overlying beds of quicksand. Before 1914, the United States made most of its sulfuric acid from imported and domestic pyrite and from by-product sulfur dioxide from copper and zinc smelters. The mining of sulfur in Texas and Louisiana by the Frasch process was increased, starting around 1914, to such an extent that it provided for most domestic needs and entered world markets. In recent years a major source of elemental sulfur is H_2S , which is a by-product of the desulfurization of sour (i.e. sulfur-containing) natural gas and sour crude oil. Canada, France, and the United States are the largest producers of recovered sulfur.

In 1980, world production of sulfur in all forms amounted to $54.6 \times 10^6 \text{ t}$,^{1a} of which 26.1 percent was Frasch-produced, 32.2 percent recovered, 5.5 percent other elemental, and 36.2 percent obtained from nonelemental sources such as pyrites and smelter gases.

USES AND ECONOMICS. The United States produced $13 \times 10^6 \text{ t}$ of elemental sulfur in 1981. Of this, 48.8 percent was by the Frasch hot water process, 17.7 percent from oil refineries, and 15.4 percent by desulfurization of natural gas. Net imports were $1.13 \times 10^6 \text{ t}$. Frasch production, which in 1982 represented 53 percent of the U.S. supply, is predicted to fall to 29 percent by 1990 as the amount of recovered sulfur continues to increase. Other sources expected to be of future importance are: shale oil, coal gasification, synthetic fuel projects,

¹Duecker and West, *Manufacture of Sulfuric Acid*, ACS Monograph No. 144, Reinhold, New York, 1959 (most important for both sulfur and sulfuric acid, many references); *Sulfur and SO_2 Developments*, Chemical Engineering Progress Technical Manual, 1971.

^{1a}t = 1000 kg.

and gypsum² (or anhydrite). World stockpiles of sulfur exceed 26×10^6 t with Saudi Arabia, Poland, and Iraq likely to increase the oversupply as new sulfur supplies are tapped there.

Over 90 percent of the sulfur used is converted to sulfuric acid, but other industrial uses abound. Some of these are: in the manufacture of wood pulp, carbon disulfide, insecticides, fungicides, bleaching agents, vulcanized rubber, detergents, pharmaceuticals, and dyestuffs. Among some new uses being studied are: (a) as an extender for paving asphalt, (b) sulfur concretes and mortars, (c) plant and soil treatment, (d) sulfur-alkali metal batteries, and e foamed sulfur insulation³.

MINING AND MANUFACTURE OF SULFUR

Elemental sulfur ores were mined manually before the development of the Frasch process. The sulfur in these ores was then concentrated by burning part of the sulfur in piles to melt the remainder, drawing off the liquid, and casting it into molds. The development of the Frasch process made such mining impossibly expensive. Native sulfur deposits are mechanically mined in Eastern bloc countries, and to a lesser extent in other countries. Marketable sulfur is produced by heating in autoclaves, drawing off the liquid, and casting it into large blocks from which it is subsequently reclaimed as a solid. Some is converted to flowers of sulfur by distillation (sublimation).

Ores (from volcanic and similar deposits), without upgrading, can be roasted (burned) to make sulfur dioxide gas, which is used to produce sulfuric acid and for other purposes. Elemental sulfur is also produced by removing hydrogen sulfide from natural and refinery gases with absorbents such as mono- and/or diethanolamines. The hydrogen sulfide is then converted to elemental sulfur by the Claus or modified Claus process. This process is described under sulfur from fuel gases.

FRASCH PROCESS. The major tonnage of all the elemental sulfur of the world has been obtained from the sulfur-bearing porous limestones of the salt-dome caprocks of Texas, Louisiana, and Mexico by the Frasch process. As early as the late 1890s, Herman Frasch devised his ingenious method⁴ of melting the sulfur underground or under the sea and then pumping it up to the surface. Ordinary oil-well equipment is used to bore holes to the bottom of the sulfur-bearing strata, a distance underground from 150 to 750 m. A nest of three concentric pipes, varying in size from 3 to 20 cm in diameter, passes through the sulfur-bearing stratum and rests on the upper portion of the barren anhydrite, as shown in Fig. 4.1. A 10-cm pipe passed through the 20-cm one so that an annular space exists between the two, extends nearly to the bottom of the sulfur-bearing rock, and rests on a collar that seals the annular space between the 20- and the 10-cm pipes. An air pipe, 3 cm in diameter, inside the others, reaches to a depth slightly above the collar mentioned above. The 20-cm pipe is perforated at two different levels, one above and the other below the annular collar. The upper set of perfora-

²Higson, CaSO_4 as a Raw Material for Chemical Manufacture, *Chem. Eng. News* 29 (43) 4469 (1951); Hill, Schonand, and Zergiebal, *Ind. Eng. Chem.* 49 (8) 1204 (1957).

³Davis, Sulfur: New Uses Needed, *Chem. Eng.* 79 (17) 30 (1972).

⁴Sulfur Mining at Newgulf, *Chem. Eng.* 48 (3) 104 (1941); Haynes, *The Stone that Burns*. Van Nostrand, New York, 1970.

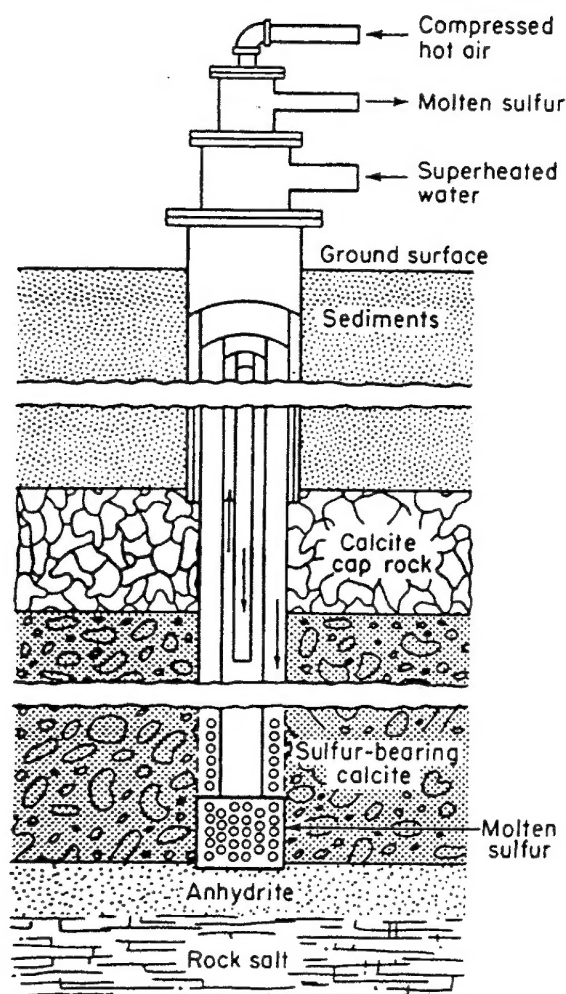


Fig. 4.1. Schematic diagram of the Frasch process for mining sulfur. (McGraw-Hill Encyclopedia of Science and Technology.)

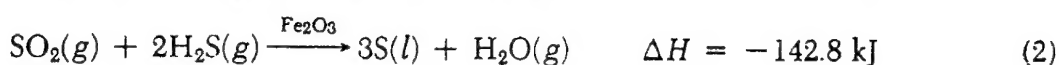
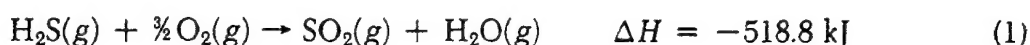
tions permits escape of the hot water, and molten sulfur enters the system through the lower perforations.

For operation of the well, hot water at about 160°C is passed down the annular space between the 20- and the 10-cm pipes. It discharges through the perforations into the porous formation near the foot of the well. The sulfur-bearing rock around the well through which this water circulates is raised to a temperature above the melting point of sulfur, about 115°C . Molten sulfur, being heavier than water, sinks and forms a pool around the base of the well, where it enters through the lower perforations and rises in the space between the 10- and the 3-cm pipes. The height to which the sulfur is forced by the pressure of the hot water is about halfway to the surface. Compressed air forced down the 3-cm pipe aerates and reduces the density of the liquid sulfur so that it will rise to the surface. The compressed air volume is regulated so that the production rate is equalized with the sulfur melting rate in order not to deplete the sulfur pool and cause the well to produce water. Water must be withdrawn from the formation at approximately the same rate as it is injected to prevent a buildup of pressure to the point where further injection would be impossible. Bleed wells for extracting water from the formation usually are located on the deeper flanks of the dome to withdraw the heavier cold water which accumulates there. Water heating capacities of existing power plants are as high as 38,000 t/day. The amount of water required to produce 1 t of sulfur depends on the richness of the deposit and other factors. Requirements may range from 4 to 50 t per metric ton of sulfur mined.

On the surface, the liquid sulfur moves through steam-heated lines to a separator where

the air is removed. The sulfur can be either solidified in large storage vats or kept liquid in steam-heated storage tanks. More than 95 percent of all U.S. sulfur is shipped as a liquid in insulated tank cars, tank trucks, and heated barges or ships. This reduces freight costs and gives the purchaser much purer sulfur.

SULFUR FROM FUEL GASES. Increasingly hydrogen sulfide is being removed⁵ during the purification of sour natural gas, coke-oven gas, and from petroleum refinery gas by dissolving it in potassium carbonate solution or ethanolamine, followed by heating to regenerate it (see Chap. 6). The hydrogen sulfide thus produced is burned to give sulfur dioxide for sulfuric acid. However, the majority is converted to elemental sulfur by various modifications of the original Claus process, for which the reactions are:



The use of this process is illustrated in the flowchart of Fig. 19.2. Air pollution regulations require new plants to attain over 98 percent conversion, and the province of Alberta, Canada, is asking for 99.5 percent conversion.⁶ To meet the new emission regulations, a number of processes have been developed for cleaning the residual sulfur values from the tail gases of recovery plants.⁷ A process used to treat the tail gases is shown in Fig. 4.2. Approximately one-half of the world production of elemental sulfur is made by gas treatment.

Other existing or potential sources of sulfur include coke-oven gases and synthetic crude oils from tar sands or shale oil. Tar sands and shale oil plants are being operated in Canada and Brazil.⁸ Very little sulfur is presently recovered from coal, but efforts to reduce sulfur dioxide emissions by developing clean fuels from coal could produce significant amounts in the future. Coal cleaning technology can remove about half of the sulfur in coal, but the organic sulfur can be removed only by gasification, liquefaction, and hydrogenation processes. Several such processes are in various stages of development.⁹ Where sulfur-containing

⁵Brennan, Amine Treating of Sour Gas: Good Riddance to H_2S , *Chem. Eng.* 69 (22) 94 (1962); Heppenstall and Lowrison, The Manufacture of Sulfuric Acid, *Trans. Inst. Chem. Eng.* 31 389 (1953); Sulfur from H_2S , *Chem. Eng.* 59 (10) 210 (1952); Duecker and West, op. cit. chaps. 4, 5, and 9; Estep, McBride, and West, *Advances in Petroleum Chemistry and Refining*, vol. VI, chap. 7, Interscience, New York, 1962.

⁶Rowland, *Oil Week*, Oct. 23, 1974, p. 9.

⁷Aquitane Cleans Claus Tail Gas with Sulfreen Unit, *Oil Gas J.* 70 (26) 85 (1972); Davis, Add-on Process Stems H_2S , *Chem. Eng.* 79 (11) 66 (1972); Barry, Reduce Claus Sulfur Emission, *Hydrocarbon Process.* 51 (4) 102 (1972); Chalmers, Citrate Process Ideal for Claus Tail-gas Cleanup, *Hydrocarbon Process.* 53 (4) 75 (1974); Ludberg, "Removal of Hydrogen Sulfide from Coke Oven Gas by the Stretford Process," paper presented at the 64th annual meeting of the Air Pollution Control Association, Atlantic City, N.J., 1971.

⁸Pattison, Oil Begins to Flow from Canadian Tar Sands, *Chem. Eng.* 74 (24) 66 (1967); Franco, Brazil Tries New Shale Oil Process, *Oil Gas J.* 70 (37) 105 (1972).

⁹Chopey, Taking Coal's Sulfur Out, *Chem. Eng.* 79 (16) 86 (1972); *Environ. Sci. Technol.* 8 (6) 510 (1974).